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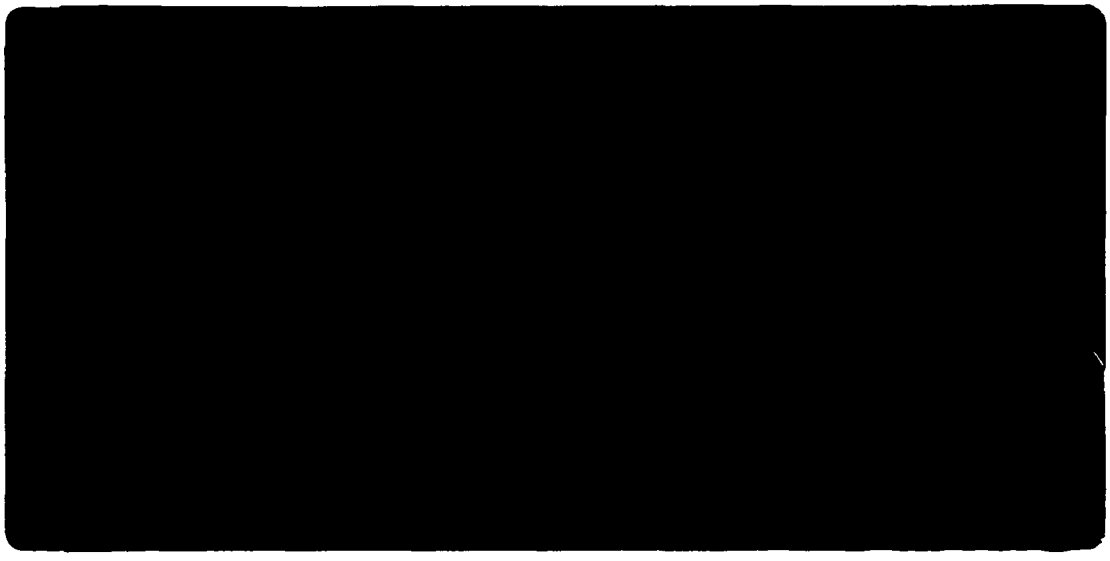

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PROPERTIES OF CHLORO-ORGANICS FORMED DURING PULP BLEACHING WITH RADIOACTIVE CHLORINE

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PROPERTIES OF CHLORO-ORGANICS FORMED DURING PULP BLEACHING WITH RADIOACTIVE CHLORINE

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ABSTRACT

Preliminary results are provided on the distribution and lipophilicity of labeled products obtained from bleaching pulp with radioactive chlorine.

KEYWORDS

36-Chlorine Octanol Mass Balance

INTRODUCTION

During the bleaching of Kraft pulp, 45-90 kg of organic material is dissolved per metric ton of pulp produced (1). Of this, 75%-90% is formed in the first two bleaching stages normally used, chlorination and extraction (2). An average of 5 kg of organically-bound chlorine results from each metric ton of pulp bleached by conventional methods. Given the environmental concerns associated with chloro-organics, it is important to understand the origin, distribution, and biological effects of these compounds. In this study we use radioactive chlorine to generate tagged chloro-organics, which can then be tracked through the system rapidly, accurately, and with high sensitivity and selectivity.

MATERIALS AND METHODS

An oxygen-delignified Southern pine Kraft pulp of kappa number 31 was used. The pulp was hand-washed and brought to 24% consistency by vacuum filtration (with recycling of filtrate). Radioactive chloride ($^{36}Cl^-$) as HCl was purchased from du Pont. Scintillation counting was done on a Beckman 3704 instrument.

Preparation of Radioactive Chlorine

Molecular chlorine is in equilibrium with ionic species through the processes

$$Cl_2 + H_2O = HOCl + HCl$$

$$Cl_2 + Cl^- = Cl_3^-$$

Thus, if radioactive chloride ion is added to an aqueous chlorine solution, the isotope will rapidly equilibrate to give labeled chlorine. In order to verify this, a chlorine solution containing $^{36}Cl^-$ was added to an aqueous solution of phenol at pH 11. The chlorination of phenol is rapid, and if radioactive chlorine was formed, as expected, then a large fraction of the isotope would be associated with the chlorination products of phenol.

The phenol:chlorine molar ratio used was 50:1, to ensure that most of the radioactive chlorine would be consumed. After a 30 minute reaction period, the solution was acidified with concentrated HNO_3, extracted with toluene, and counted for radioactivity.

If *all* the chlorinated products from phenol extracted into toluene, then half of the initial radioactivity would transfer to the toluene phase, with the other half remaining in the aqueous phase as inorganic chloride. We found the organic:aqueous phase distribution to be 40:60. Clearly, the added $^{36}Cl^-$ is cycled into molecular chlorine.

Pulp:water Distribution of Chloride

Bleaching with radioactive chlorine is expected to generate products that are bound to pulp. In order to verify that the activity in pulp derives principally from organic products rather than from the radioactive chloride ion initially added, an unbleached Kraft loblolly pine pulp at 3% consistency was added to an aqueous solution of radioactive chloride. No detectable counts were lost to the pulp.

Bleaching Experiments

Bleaching experiments were conducted in a 40 mL glass vial sealed with a paraffin-coated stopper. For the chlorination stage, pulp (0.5 g. od) was added to the chlorination vessel at 3% consistency, and the mixture was maintained at 50°C for 1 hour. During Cl_2/ClO_2 bleaching, the ClO_2 was added 1 minute prior to Cl_2 addition. The extraction stage was conducted for 1 hour at 70°C and 5% consistency. The chlorina-

TABLE 1: Distribution of Radioactivity in Pulp and Effluents

percent Cl applied	percent NaOH applied	recovery[b] (%)	distribution of recovered activity (%)[a]			
			C	E	E_{pw}	pulp
3.4	40	82	80	13	2	5
	7	78	84	12	1	3
3.9[c]	40	77	82	15	1	1
	7	71	83	12	2	3
4.3	7	74	82	13	2	3

[a]C:chlorination effluent; E:extraction effluent; E_{pw}:pulp wash following extraction; [b]of total radioactivity applied; [c]23% ClO_2 substitution

tion/extraction conditions were as follows:

(i) 3.4% active chlorine applied (≈0.20 Cl_2 multiple) - 100% Cl_2; extraction stage: 40% and 7% NaOH by weight.

(ii) 3.9% active chlorine applied (≈0.23 Cl_2 multiple); 76% Cl_2 chlorine & 23% ClO_2; extraction stage: 40% and 7% NaOH by weight.

(iii) 4.3% active chlorine applied (≈0.25 Cl_2 multiple); 100% Cl_2;. extraction stage: 7% NaOH by weight.

Pulp was separated from the mixture *via* vacuum filtration. The filtrate was recycled through the pulp mat in order to simulate actual mill operating conditions and to recapture fines. The CE pulp was washed with 5 ml of 70°C distilled water prior to collection and storage. The effluents and pulps were then extracted with 1-octanol in order to determine the overall octanol:water partition coefficient of the chloro-organics.

RESULTS AND DISCUSSION

An oxygen delignified pulp was bleached with ^{36}Cl, and the activity in the effluents and pulp was counted at various stages. The results are presented in Table 1. Recoveries ranged between 74%-82%, and the loss probably reflects the escape of chlorine gas and volatile products. As expected, the bulk (80-84%) of the recovered activity was found in the C-stage effluent. Since the chloride ion generated should appear in the effluent rather than in the pulp, much of this activity is chloride. Most of the (20%) organo-chlorine remaining in pulp is extracted out in the E stage.

The activity found in the E stage (12-15% of the total activity recovered) is the same at 7% and 40% applied caustic. In order to obtain a more complete profile, the C-stage pulp from entry 3 of Table 1 (4.3% Cl applied) was extracted with various levels of caustic. The results provided in Table 2 show no real improvement in extraction efficiency beyond a charge of 7% caustic.

Partitioning into Octanol

The bioconcentration potential and narcotic toxicity of many organic compounds increase with their octanol:water partition coefficient (K_{ow}). In order to determine what fraction of the pulp and process liquids were octanol soluble, each C-stage fraction in Table 1 was extracted with an equal volume of octanol.

The results provided in Table 3 show that a surprisingly small fraction of the products partitions into octanol. Admittedly, the C-stage contains the bulk of the inorganic chloride generated, which does not partition to octanol.

TABLE 2: E Stage Extraction Efficiency vs. Applied Alkali

percent caustic applied	activity recovered (%)
0	5
1	6
2	7
4	8
7	14
40	15

However, even if 90% of the counts in the aqueous phase is attributed to chloride (3), the averaged K_{ow} for the organics is still much less than one. Hence, taken *collectively*, the chloro-organics strongly favor the aqueous phase and are not likely to bioconcentrate. Individual components may, of course, bioconcentrate appreciably.

No radioactivity was released when the pulp fraction in Table 1 was extracted with octanol. This confirms that most of the chloro-organics in pulp are inextricably bound, and are presumably not bioavailable.

Our present objective is to separately follow the products from Cl_2 and ClO_2 bleaching by labeling first one, and then the other oxidant.

TABLE 3: Octanol:Water Partitioning of C-Stage Labeled Species

percent chlorine applied	NaOH applied (%)	K_{ow}
3.4	40	0.012
	7	0.011
3.9[a]	40	0.013
	7	0.019
4.3	7	0.006

[a] 23% ClO_2 substitution

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